

EXHIBIT "A"

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of: El-Shall et al.

Application No.: 10/725,158

Examiner: Hruskoci

Date Filed: December 1, 2003

Group: 1724

For: TREATMENT OF SPENT PULPING LIQUOR WITH LIGNIN SEPARATION TO RECOVER ALKALI PULPING CHEMICALS IN MANUFACTURE OF PAPER PULP

CERTIFICATE UNDER 37 CFR 1.8(a)

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Neil R. Jetter

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RULE 132 DECLARATION

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I, Harrison R. Cooper, declare as follows:

1. I am familiar with patent application No. 10/725,158 entitled "TREATMENT OF SPENT PULPING LIQUOR WITH LIGNIN SEPARATION TO RECOVER ALKALI PULPING CHEMICALS IN MANUFACTURE OF PAPER PULP " and the subject matter described therein.

2. I hold a doctorate in chemical engineering from University of Southern California which was awarded in 1962. Since 1990, I have worked regularly with pulp

processing including black liquor treatment. I am the president of Bountiful Applied Research Corporation (hereafter "Bountiful"), a Corporation focused on new technologies including those to simplify use of agro residues as pulp and paper raw material. Bountiful is the owner of U.S. Pat. No. 6,632,327 to El-Shall. Although I currently do not own an interest in U.S. patent application 10/725,158, based on negotiations to date with the University of Florida I am hopeful that Bountiful will gain an ownership interest and/or licensing rights in subject matter described therein.

3. I have reviewed the Office Action dated June 2, 2004 and references cited therein. I do not agree with the determination in the Office Action that that the claimed invention which utilizes phosphoric acid derived from phosphate containing material such as phosphate rock for treating spent alkaline pulping liquor is obvious based on WO 98/54400 El Shall ("Shall '00") in view of U.S. Pat. No. 5,824,132 to Kopyleva et al. ("Kopyleva").

4. Shall '00 discloses a method of treating spent alkaline pulping liquor generally utilizing sulfuric acid for acidulation. Phosphoric acid is mentioned once as a possible acid for acidulation, but no mention is made of utilizing phosphate containing material, such as phosphate rock to generate the phosphoric acid. Kopyleva describes a better way to process phosphate mineral to phosphoric acid applicable to the manufacture of phosphate fertilizers, but the underlying process of using phosphate rock to generate phosphoric acid (referred to as "wet processing") is at least 80 years old. Kopyleva does not mention treatment of spent alkaline pulping liquor.

5. To accommodate high cost of suitable high-grade phosphate rock as raw material for beginning the process of fertilizer manufacture, acidulation of phosphate rock

proceeds in a multi-step acidulation process to ensure maximum extraction of phosphoric acid from the rock. In such a process, phosphoric acid and impurities in the rock are solubilized together in water and are added back successive times to the phosphate rock for treatment with sulfuric acid repeated times. The purpose of this process is to maximize recovery of phosphate from the source material, and also to obtain the highest possible concentration of phosphoric acid in the product to minimize energy demands of evaporation to meet acid concentration requirements for fertilizer manufacture. Although such a recycling process improves the amount of phosphoric acid extracted from the rock and results in increased acid concentration in the product, the resulting liquid typically decanted also becomes laden with an enhanced level of impurities due to the accompanying increased dissolution of impurities. Impurities cause high viscosity and often precipitate in the stored product acid generated by the process. As a result of the impurity related problems, making phosphoric acid for treatment of black liquor by this process is disadvantageous.

6. The claimed invention solves chemical recovery as part of the black liquor problem in a novel a non-obvious manner through phosphoric acid derived from phosphate containing material, such as low grade rock and other relatively inexpensive sources of phosphate mineral. By minimizing and preferably avoiding acidulation recycling, the resulting impurity level in the acid derived is kept low, thus reducing introduction of extraneous soluble matter into the pulping liquor being treated and thereby suppressing the potential for there subsequent precipitation. The relatively dilute phosphoric acid generated is surprisingly effective when mixed with black liquor to cause separation of lignin from the black liquor. In a preferred embodiment, the Shall 00 process including a water soluble,

surface active polymeric agent for coagulating lignin is also applied. Solid products generated from the claimed process include tricalcium phosphate TCP which can be reused to generate phosphoric acid or slow release fertilizer, depending on the pH at which precipitation of mineral takes place.

7. The claimed invention also solves a long felt need and has already been greeted with significant commercial interest. Sulfuric and other strong acids have been known for decades as capable of precipitating lignin for black liquor treatment, but the method did not begin to become practical until the introduction of the Shall 00 process. Even with the Shall 00 process, the precipitation of lignin was not economically advantageous, particularly for small paper mills. Specifically, there is a long felt need for cost-effective black liquor treatment method particularly suitable and applicable to small agro fiber paper mills, as evidenced by the failure of numerous past attempts to resolve this requirement over many years of effort. Historical experience at Rakta Paper Company in Egypt and past work in this field by the Central Pulp and Paper Research Institute in India are examples of how previous work to deal with black liquor recovery on small-scale resulted in a succession of failures. I am also aware of a long list of research efforts with black liquor to recover soda caustic and produce marketable lignin organic products. Many processes developed in this effort have been clever and some are ingenious. However, none have met needs of the industry for reasons as being excessively costly in capital and/or operation, or embodied other negative aspects such as producing by-products having little or no marketable value.

The table below summarizes previously advanced process technologies which attempted to provide practical treatment and chemical recovery methods applicable to small

agro fiber paper mills.

ALTERNATIVE BLACK LIQUOR TREATMENT PROCESSES

Process Name Year Ref. Source

Comments and Notes

CONOX	1997	2.	Finland	Evaluation in India indicated cost can't be justified.
Granit	1995	3.	Switzerland	Requires sale of lignin derivatives to new markets.
MTCI	1996	4.	U. S. A.	Silica in liquor prevents practical use of evaporation.
Arbokem	1992	6.	Canada	Digestion is with potassium alkali; liquor with lignin becomes fertilizer distributed over agricultural lands.
DARP	1990	6.	Sweden	Ferrite process, technically complex and costly.
Indirect Gasification	1986	1.	Germany	Process proved too high in capital cost and silica problems prevented practical application.
Desilication and Conventional Recovery	1980	1.	India	High capital cost is determined as excessive for use by small agro fiber mills.

REFERENCES

1. Rangan, S. G., and G. Rangamannar, "Environmental Aspects of Small Agro Residue Pulp Mills: Recovery and Treatment of Waste Liquors", Proc. TAPPI Pulping Conference, San Francisco, CA, October 1997; publ. Technical Association of Pulp and Paper Industries, Norcross, GA.
2. Myreen, B, "A Novel Recovery Process for Straw Pulp Mills", publ. in "Know-How Wire -Jaakko Poyry Magazine", January 1998, No. 1, pp. 18-21.
3. Escudero, E., "Semichemical Cereals Straw Pulp, with Sulphur Free Lignin Recovery - A Clean and Profitable Process", Paper Technology (U.K.), Sept. 2000, pp. 32-8.
4. Rockvam, L. N., "Spent Liquor Steam Reforming and Recovery", Proc. 1995 Int. Chemical Recovery Conference, Toronto, Ontario, Canada, Apr. 1995.
5. Wong, A., "New Direction in Industry Development and Environmental Protection for Non-Wood Pulp Mills in Developing Countries", Proc. 2nd Int. Non-Wood Fibre Pulping and Papermaking Conf., Shanghai, China, April 1992.
6. Rao, N. J. and Kumar Ram, "Ferrite Recovery Process - A Promising Alternate for Small Paper Mills", India Pulp & Paper Technology Ann., Sept. 1987, pp. 3-4.

8. S. G. Rangan and G. Rangamannar conducted a detailed review of technologies studied and specifically tested in India toward determining a solution to the black liquor environmental problem (Ref 1). Rangan describes the many Indian black liquor

projects and their shortcomings. In their presentation to the TAPPI 1997 Pulping Conference, it was stated "The single biggest technical problem, which has so far eluded solution for small paper mills, is the absence of a dependable, economically viable chemical recovery system." Until advent of the claimed process, particularly when coupled with the Shall 00 process, I can affirmatively state that the situation has changed little to date.

9. CONOX has a currently active black liquor treatment technology developed in Finland with a demonstration plant built in China. The process was investigated by the India industry (through the India Agro and Recycle Paper Manufacturer's Association), but was turned down as not realistic because of high capital and operating costs.

10. Granit's pressure oxidation process is being used at a small straw pulp mill in France where its cost was subsidized by the European Union. Although heavily promoted in recent years, there has been no industry acceptance as it requires paper industry users to sell chemically modified lignin as a valued byproduct in order to achieve a sensible economic outcome.

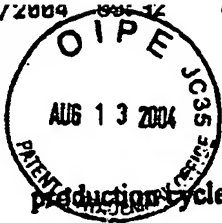
11. The MTCI steam reformer fluidized bed reactor system as applied previously in India requires black liquor to be concentrated by evaporation for processing to low calorie fuel gas used to drive combustion turbines for cogeneration power (Ref 4). Alkali recovery is made from the fluidized bed. The process is commercial for low silica kraft black liquor, but is thwarted by silica contained in the black liquor causing concentration by evaporation to be impractical. However, I consider the steam reformer to be cost-effective as means for power

production when gasifying lignin separated from black liquor by the Shall 00 process, thereby avoiding evaporation with its difficulties from silica, and enabling alkali recovery to be carried out by the claimed process.

12. The DARP ferrite process was developed in Sweden. A pilot plant was assembled and operated at CPPRI in Saharanpur beginning in 1990 (Ref. 6). A commercial plant was installed during early 90's at the Fredericia straw pulp mill in Denmark, but never came to proper operation with result the company eventually was not allowed to continue operating.

13. Because the invention solves an important long felt need, the invention has been greeted with high levels of commercial interest. For example, A Memorandum of Understanding was recently entered between the University of Florida and Central Pulp & Research Institute (CPPRI) Saharanpur, India. I expect the CPPRI deal expected to close shortly was based on a preliminary financial analysis for typical agro fiber paper mills applying the claimed invention.

An economic analysis of the process is based on an assumption that phosphate and pulping chemical losses can be maintained to about ten per cent of that contained in the original process stream, and purchase prices of sulfuric acid and lime, the primary ingredients for black liquor recovery treatment remain in accord with present-day experience. The financial projection includes sales revenue of byproducts at nominal prices, but the main benefit is derived from minimizing need for replacing pulping chemical (soda caustic) in the



production cycle. From this it is estimated that the net benefits to a paper company will be in range of US \$100 per ton of paper produced by comparison to operating with no recovery as is presently done.

For a 50,000 ton per year production level (approximate production rates at Rakta and also Satia Paper Mills in India where the demonstration treatment plant is to be installed), additional revenue yield will be about \$5,000,000 annually above treatment costs (without considering capital investment amortization).

14. I further state that all statements made herein are of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with my knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.


Dr. Harrison R. Cooper

8-9-2004

Date

1.3 PHOSPHORIC ACID PRODUCTION: PARTICULARITIES OF THE WET PROCESS TECHNOLOGY

By its nature, wet process technology conserves most of the impurities found in the original phosphate ore, which are then included in the phosphoric acid produced. Consequently, the variety of the phosphate ores influences not only the process used but also the composition and characteristics of the phosphoric acid produced.

Wet process phosphoric acid technology, which will be described in the next sections, essentially comprises sulfuric acid attack and separation of the phosphoric acid produced from the calcium sulfate crystals resulting from the reaction. Both the attack and the separation, which is effected by filtration, are considerably affected by the nature of the ore and its impurities.

Besides calcium phosphate, the phosphate ores contain 10-15 major impurities and another 16 or so trace elements.* Organic matter, also present in many ores, is not included in this estimation. Each element contained in the ore has its individual transfer coefficient into product acid and waste solids.

Without enumerating all the effects on processes and economics due to the impurities, some of the more common are:

1. *Effect on crystallization:* The calcium sulfate qualities, due to the presence of the various impurities, affect filtration rates by a factor of 4 from one phosphate ore to another.
2. *Scaling:* Vessels and pipework are subject to deposits of various kinds. Heat transfer coefficients, pressure drop in pipework, are subject to heavy alterations.
3. *Sludge formation:* Some impurities are subject to delayed precipitation in the stored product acid or the final concentrated acid. These are sludges—a difficult problem for the phosphoric acid producer.
4. *Corrosion:* Despite the use of exotic alloys, pump impellers and agitator turbines can be subject to rapid deterioration by corrosion.
5. *Environmental aspects:* Acidic fluoride compounds evolve from reaction vessels and concentration plants. They have to be recovered and combined to produce salable or at least harmless compounds. Trace elements such as cadmium have aroused great concern, and in the case of specific phosphate rock sources, have affected their sales patterns considerably.

*Mainly heavy metals and rare earth elements.

Many impurities, despite tedious procedures, cannot be analyzed quantitatively with accuracy, either from the phosphate rock or from the phosphoric acid produced. For example, it is possible for a 15 to 25% absolute deviation in iron and aluminum contents, respectively, to be found within the same ore sample as measured by different laboratories.

If the problems listed above characterizing phosphoric acid wet process technology are not discouraging enough, consider, too, the complications from dust, foam, and so forth.

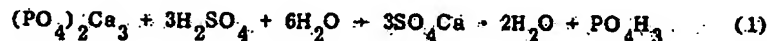
From the foregoing it is obvious that the science of phosphates and the technology of phosphoric acid is somewhat esoteric. Words such as "technology" or "calculation," in this case, have to be employed very carefully. Sometimes traditional calculation methods can be used and sometimes one has to rely on experience and accept a simple estimation based on similar cases.

An understanding of what and how to calculate in phosphoric acid technology is the objective of this book. We hope the reader will derive some advantage from the many years the various authors have spent in the dust and effluent gases of phosphoric acid plants, watching filter cakes and plugging pipes!

Like human beings, phosphates are fascinating; they never behave consistently. They like to be treated differently every time. Once you are married, even if only to phosphates, you need to use a fresh approach day by day.

1.4 HISTORY OF PHOSPHORIC ACID CHEMISTRY AND PRODUCTION USING THE WET PROCESS

The production of phosphoric acid by means of the wet process began to be developed intensively following World War II. As a simple transformation of calcium from a phosphate to a sulfate, the reaction is



The reality is, in fact, not as simple because of the technology that must be used. The phosphate attack and the formation of the calcium sulfate take place on their own, so to speak, but the calcium sulfate crystals (gypsum or hemihydrate) then have to be separated from the phosphoric acid that is produced.

This separation must be thoroughly completed since, at the price of phosphoric acid, even a small loss at the filter will show up quickly in the economics of the operation. A properly functioning plant will, under normal running conditions, lose 0.5% of the acid during filtration. This percentage is increased by startups, and

the measured average should not exceed 1% (measured average of the acid losses in the liquid effluents that accompany the rejected gypsum, which does not include the losses of combined P_2O_5 contained in the gypsum).

Good separation at the filter is achieved when crystallization at the reactor is "good." This type of crystallization has not, however, proven easy to perfect; several decades of work have been required. The science of "good crystallization" in a phosphoric medium has been perfected only by means of experimentation, which explains its long, slow evolution. In mixing phosphate with sulfuric acid, early producers were forced to conclude that great caution was necessary in this operation on an industrial scale, for a number of reasons.

The phosphate, being very porous, reacts extremely quickly without allowing the sulfate crystals to grow in a regular manner. The reaction is very exothermic, and the calories must be evacuated since, if the medium is too hot, no more $SO_4Ca \cdot 2H_2O$ is created; but instead, semi- or hemihydrate or anhydrous material forms, which can recrystallize on the filter. Also, if the reaction becomes too hot, the phosphate is blocked in sulfate shells (coating) and the attacking yield is bad (large-scale losses of unattacked P_2O_5).

Similarly, one has to work in a relatively diluted medium (27-30% with dihydrate processes, 40-45% for most cases with hemihydrate processes). With growing P_2O_5 concentration, viscosity increases dramatically and prohibits economical filtration. Mass transfer and crystallization quality can be affected considerably.

The first wet process phosphoric acid plants built between the World Wars I and II generally produced between 25 and 50 tons of P_2O_5 per day. The problems of mixing and agitation were poorly understood, so that the reactive media were not really homogeneous and were highly supersaturated. The poor crystals were therefore separated by decanting, an operation necessitating huge volumes of equipment.

I was able to see one of these installations before it was demolished. The reagents were mixed in premixers fitted with great wooden stirrers turning slowly and the reactions were completed in enormous reaction tanks. The gypsum was separated by decanting. The total size of the operation meant that 700 m³ was needed to produce 20 tons of P_2O_5 per day in the form of 25% acid by using the high-grade phosphates available at that time. To reduce the problem of supersaturation in the premixers, slurry was recycled after the reactions has been completed in a long series of reaction tanks.

The problem of calcium sulfate crystallization within media with a greater concentration of P_2O_5 has fascinated many researchers and as far back as 1930, Nordengreen took out patents for the manufacture of more concentrated (40% P_2O_5) phosphoric acid by means

assessment. The following criteria concern the most common impurities. Detailed evaluation of the effects of the impurities will be seen in Sections 2.2.5, "Effect of Impurities," 3.1.6, 3.5, 5.7, 6.22, 8.1-8.5, 10.2, and Appendix A. The preliminary criteria for appreciating the quality of a rock depends on the final product we want to manufacture. To produce phosphoric acid, the main criteria for phosphate ore are:

P₂O₅ content or TPL (BPL) grade: when above 33% P₂O₅ (72 TPL), up to 38% P₂O₅ (83 TPL), or even 39% (85 TPL) the rock is considered as a high grade. The current grade is 30-33% P₂O₅ (65-72 TPL). From 26 to 30% (57-65 TPL) is considered low grade. There is very few commercial grade below 26% P₂O₅ (56 TPL).

CaO content: affects the sulfuric acid consumption. Each percent of CaO needs an equivalent of 17.5 kg H₂SO₄ per ton of rock. High CaO has an economic effect only. Relatively pure acid can be produced from ore containing very large amounts of calcite.

Fluorine: usually occurs in sedimentary rock as 10% of the P₂O₅ weight. Fluorine can be a corrosive component if not enough reactive silica is also present. With a high sodium content (1% or more) most of it will precipitate during the phosphoric acid reaction. About half the remaining part in the product acid escapes when concentration by evaporation is operated.

SO₃ (sulfates): only a dead weight. However, the existing SO₃ in phosphate rock will save the corresponding amount of sulfuric acid during the acidulation.

Chlorine: an undesirable impurity, because of corrosion danger. Usually becomes dangerous beyond 0.1%, its corrosive action is enhanced by interactions with other impurities (FH, SO₄H₂). **SiO₂:** as quartz, only a dead weight. Reactive silica (from clays, for example) is needed to combine with fluorides to prevent corrosion. However, highly reactive silica will depress filtration rates (use flocculants).

Al³⁺ and Fe³⁺: not a problem during phosphoric acid manufacture but afterward when using the phosphoric acid. Sludge formation with the concentrated acid; builds water-insoluble components in the phosphate fertilizer. Usual merchant-grade limit to be considered:

$$0.02 < \frac{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}{\text{P}_2\text{O}_5} < 0.0825$$

Too low an aluminum content is not welcomed either, because of increased corrosion and lower physical properties with fertilizer products downstream.

MgO: stays with the acid phase. Increases viscosity strongly. MgNH₄P₂O₇ formation when the acid is ammoniated. Difficult manufacture of superphosphoric acid beyond a certain threshold (0.6% in rock).

NaO: precipitates as Na₂SiF₆ from the acid.

Organics: foaming during reaction, dark cloudy solids suspended in product acid.

Trace elements: can affect crystallization and recrystallization by adsorption on crystal surfaces (can be dramatic in case of non-dihydrate processes with recrystallization). They may have toxic effects in specific final products (animal feed or fertilizer).